EP 31322 (2)

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 869 406 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
07.10.1998 Bulletin 1998/41

(51) Int Cl.^{6}: **G03G 15/20**

(21) Application number: **98302295.5**

(22) Date of filing: **24.03.1998**

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **01.04.1997 US 831990**

(71) Applicant: **TEKTRONIX, INC.**
Wilsonville, Oregon 97070-1000 (US)

(72) Inventor: **Ni, Beta Y.**
Sherwood, Oregon 97140 (US)

(74) Representative: **Lawrence, Malcolm Graham et al**
Hepworth, Lawrence, Bryer & Bizley
Merlin House
Falconry Court
Baker's Lane
Epping Essex CM16 5DQ (GB)

(54) Fusing apparatus employing multi-fuctional toner release agent

(57) The invention relates to a fuser member (1,9) and an apparatus with a fuser member for fusing electrophotographic toner images of various colors (14, 140) to a substrate (12, 120). The fuser member (1, 9) includes a base member (4, 40) coated with a mixture of at least a first and a second polymeric release agent. The first and second polymeric release agents each have a functional group selected from hydroxy, epoxy, carboxy, amino, isocyanate, thioether, or mercapto. The functional group of the first polymeric release agent is different from the functional group of the second polymeric release agent. The functional groups of the first and second polymeric release agents occupy through reactive binding sites on the surface of the base member.

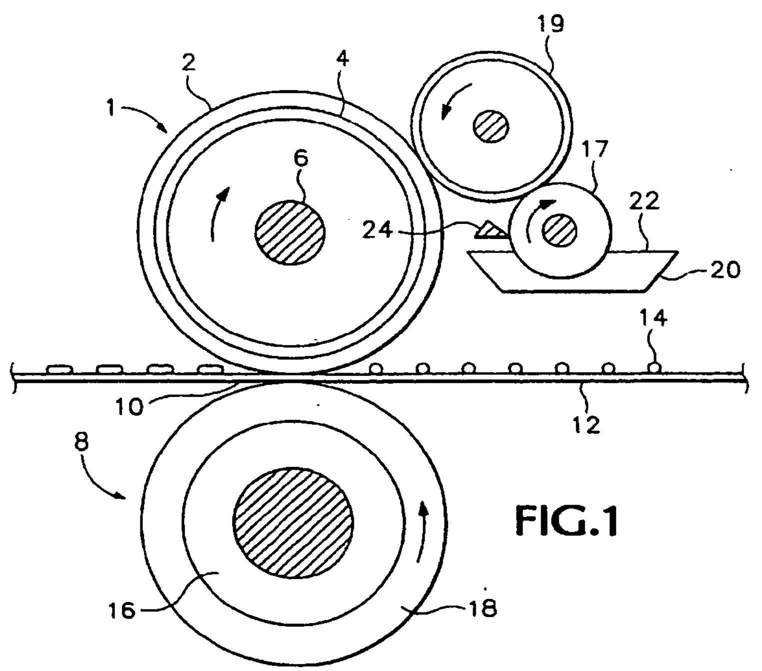

FIG.1

EP 0 869 406 A2

Description

The invention relates generally to printing and reproducing, copying, or duplicating and more particularly to a fuser member, an apparatus with a fuser member, and a system for fusing electrophotographic toner images of various colors.

A typical electrophotographic apparatus is a copier or printer that forms an electrostatic latent image upon a photosensitive member and the latent image is subsequently rendered visible by the application of electroscopic thermoplastic resin particles or toner. In a reproducing apparatus like a copier or duplicator, the light image of an original to be copied is recorded in the form of the electrostatic latent image on a photoconductive surface like a drum. In a laser printer, for example, the latent image is typically generated by data supplied from a computer system on a photoconductive surface. Next, the photoconductive surface is charged and exposed to a light image to selectively expose the surface and record the input information in the form of a latent electrostatic image. A thermoplastic resin, commonly referred to as a toner, is then applied to the photoconductive surface rendering the latent image visible. The visible toner image is in a loose powdered form and can be easily disturbed or destroyed. The toner image is usually fixed or fused upon a support which may be a photomember itself or other support substrate such as plain paper, gummed labels, or transparencies such as polycarbonate, polysulfone, Mylar, and the like. Mylar is a trademark of E.I. duPont de Nemours & Company.

The use of thermal energy for fixing toner images onto a support substrate is known. In order to fuse electroscopic toner material onto a support surface permanently by heat, it is necessary to elevate the temperature of the toner material to a point at which the constituents of the toner material coalesce and become "tacky". Typically, thermoplastic resin particles are fused to the substrate by heating to a temperature of between 90°C to about 170°C or higher depending upon the softening range of the particular resin in the toner. This heating causes the toner to flow to some extent into the fibers or pores of the support substrate, e.g., paper. Thereafter, the toner material is allowed to cool and as it cools, solidification of the toner material causes the toner material to be firmly bonded to the support.

Several approaches to thermal-fusing of electroscopic toner images have been described in the prior art. These methods include providing the application of heat and pressure substantially concurrently by various means. Examples of this method include a pair of rollers maintained in pressure contact, and a belt member in pressure contact with a roller. Heat may be applied by heating one or both of the rollers, plate members, or belt members. Coalescence of the toner particles takes place when the proper combination of heat, pressure, and contact time are provided. The balancing of these parameters to bring about the fusing of the toner particles is known in the art, and the parameters can be adjusted to suit particular machines or process conditions.

During the fusing operation in which heat is applied to cause thermal-fusing of the toner particles onto a support substrate, both the toner image and the substrate are passed through a nip or arch formed between the roller pair, or plate or belt members. The concurrent transfer of heat and the application of pressure in the nip affects the fusing of the toner image onto the substrate. It is important in the fusing process that no displacement takes place of the toner particles from the substrate to the fuser member during normal operations. In most instances, however, as the powder image is tackified by heat, part of the image carried by the support substrate will stick to the surface of the plate or roller. Thus, the tackified image partially removed from the first substrate will partly transfer to the next substrate from the surface of the plate or roller and at the same time part of the tackified image from the next substrate adheres to the heated roller or plate. This process is commonly referred to in the art as "offset" or "hot offset".

To ensure and maintain good release properties of the fusing system, it is desired to provide a fusing surface which has a low surface energy to provide the necessary release. Thus, improvements in the fusing process have included fusing toner images by forwarding the substrate bearing the image between two rollers at least one of which was heated, the rollers contacting the image being provided with a surface such as a thin coating of tetrafluoroethylene resin, commonly referred to as Teflon, and a release agent, for example, silicone oil film continuously applied to the surface of at least one of the rollers to prevent toner offset. Teflon is a trademark of E.I. duPont de Nemours & Company. Bare metal base members such as rollers having functionalized polymeric release agents upon their surfaces are also known in the art. The functionalized polymeric release agents that have shown effectiveness include mercapto-functional polyorganosiloxanes, amino-functional polyorganosiloxanes, hydroxyfunctional polyorganosiloxanes, epoxy-functional polyorganosiloxanes, carboxy-functional polyorganosiloxanes, and cyano-functional polyorganosiloxanes. These functionalized polymeric release agents have been the subject of various patents. Such polymeric release agents include U.S. Patent No. 3,883,628, (amino-functional organopolysiloxane), U.S. Patent No. 4,011,362 (carboxy-functional organopolysiloxane), U.S. Patent No. 4,029,827 (mercapto polyorganosiloxanes), and U.S. Patent No. 4,046,795 (thio-functional polyorganosiloxanes).

U.S. Patent No. 4,101,686 describes a method of fusing electroscopic thermoplastic resin toner images to a substrate by the use of a polymeric release agent of polydialkyl siloxane having functional groups selected from one of hydroxy, epoxy, amino, isocyanate, and mercapto. This polymeric release agent is distributed on the surface of a base member that is metal, for example aluminum, steel, or copper, or glass. It is postulated that the functional groups of the polymeric release agent interact with the base member to form a barrier to toner and yield a surface energy less

than the surface energy of the base member at operating temperatures. The '686 patent notes that it is critical that the polymeric release agent have functional groups that interact with the base member surface to form a thermally-stable interfacial barrier to toner. U.S. Patent No. 4,078,285 describes bare metal fuser members for pressure fusing toned electrostatic images at elevated temperatures.

The representative bare metal fuser members include those made of metal alloys of copper, copper/aluminum, copper/zinc, and the like. The fuser member is preferably used in conjunction with a backup or pressure roller structure that preferably is made of a rigid steel core with an elastomer surface. The fuser member is preferably coated with a polymeric release agent having reactive functionality such as polyorganosiloxanes having functional carboxy groups or functional mercapto groups.

The outer surfaces of the base member has also been fabricated of an elastomer surface. Typical surfaces include fluorinated ethylene/propylene polymers, elastomers that contain hexafluoropropylene as a co-monomer such as poly (vinylidene fluoride/hexafluoropropylene) or silicone elastomers as well as silicone elastomers containing low surface energy components such as fluorinated organic polymers and the like. Further, the outer surfaces of the base member have also been coated with an elastomer surface having metal-containing filler disbursed therein. U.S. Patent Nos. 4,272,179 and 4,264,181 describe a base member covered by an elastomer containing a metal, metal salt, or metal oxide, for example metals, salts, and oxides of copper, tin, silver, and lead. Examples of the elastomers that may incorporate the metal, metal salt, or metal oxide include the fluoroelastomer polymers such as the commercially available products Viton E60C, Viton B910, Viton E430, Viton A, Viton B, Fluorel 2170, Fluorel 2174, Fluorel 2176, and the like. Viton is a trademark of E.I. duPont de Nemours & Company, and Fluorel is a trademark of 3M Company.

It is believed that the functional group of the polymeric release agent interacts with the metal-containing filler disbursed in the elastomer described in the '174 and '181 patents. This interaction, it is postulated, forms a thermally stable film that releases thermoplastic resin toner and prevents the thermoplastic resin toner from contacting the elastomer material itself. It is also critical, as pointed out by U.S. Patent No. 4,264,181, that the metal filler be capable of interacting with the functional group (i.e., the hydroxy, epoxy, amino, isocyanate, carboxy, and mercapto functional group) of the polymeric release agent to interact with the metal filler of the elastomer.

With the advent of color printing and copying or duplicating, the electrophotographic imaging process has become more complex. In color electrophotographic imaging, colors are typically represented by a combination of different toners. One common industry standard is to use the colors Cyan, Yellow, Magenta, and Black. To produce an image that is not one of these representative colors, multiple toners are used. In the case of Orange, for example, Yellow and Magenta are combined to produce an Orange color. A typical method of doing this involves a multiple transfer process wherein the latent electrostatic image is formed upon a photosensitive member and the toners of different colors, for example Yellow and Magenta, are subsequently applied one at a time so that, for example, the Yellow is applied to the photosensitive member and the Yellow latent image and subsequently transferred to the substrate. Next, the Magenta toner is applied to the same photosensitive image and subsequently transferred to the substrate directly over the Yellow latent image. The combination of Yellow and Magenta produces an Orange color.

It is important to note, that each of these thermoplastic toners has various properties. The properties of the individual toners effect the interaction between the toner and the fuser member. Usually a toner contains a polymer resin, charge control agents, pigments or dies, and other small amounts of additives. Most charge control agents (CCA) are made of metal complexes. Both CCA's and pigments or dies can be chemically active and may interact with fuser material, e.g., release agents and base member, in the way that they interact with toner polymer resins to modify the triboelectric charging behaviors of the toner binders. For example, the toner wants to bond chemically to the surface of the base member, e.g., roller. It has been shown that the reaction rate of this activity goes up approximately double for every 10°C increase thus yielding a higher reaction rate at higher temperatures. Further, the chemical composition of color toners can be quite different among Black, Cyan, Magenta, and Yellow toners. The complexity of the interactions between the toner and base member along with the varied compositions of toners creates a great challenge to maintain consistent toner release performance in color printing and duplicating technologies. Therefore, the flexibility of making release agents that consistently cooperate with base members to ensure consistent release performance is an important consideration.

A fuser member and an apparatus with a fuser member for fusing electrophotographic toner images of various colors are disclosed. The fuser member includes a base member having a surface constituted of a first material and coated with a mixture of at least a first and a second polymeric release agent. The first and second polymeric release agents each have a functional group selected from hydroxy, epoxy, carboxy, amino, isocyanate, thioether, and mercapto. The functional group of the first polymeric release agent is, however, different from the functional group of the second polymeric release agent. The fuser member of the apparatus includes a base member having a surface constituted of a first material and coated with a mixture of at least a first and a second polymeric release agent. The first and second polymeric release agents have a distinct functional group selected from hydroxy, epoxy, carboxy, amino, isocyanate, thioether, and mercapto. Exemplary embodiments of the apparatus are printing, facsimile, and copying or duplicating apparati.

The functional groups of the mixture of the first and second polymeric release agents are complementary to the first material of the base member and react with and bind to a sufficient number of available binding sites on the surface of the base member. By occupying the binding sites, the release agents prevent various toners from binding to the base member surface and being offset onto the surface of the base member. In accordance with the invention, a mixture of two or more polymeric release agents having distinct functionalities has proven effective to occupy the available binding sites on the surface of the base member. This mixture of two or more release agents has proven effective to diminish the van der Waals or other attractive forces that would otherwise exist between the various color toners and the surface of the base member. Depending on the chemical characteristics of a particular base member and various color toners, the types and amounts of the functionalities of the mixed release agents are optimized to reduce interactions between the base member surface and the toners. Accordingly, the invention yields improved color quality images on a substrate by improving the surface morphology of fused toner and minimizing toner offset on the surface of the base member.

Embodiments of the present invention will now be described, by way of example, with reference to the accompanying drawings, in which:

Figure 1 is a cross-sectional planar side view of the fusing apparatus of the invention for use in a copying or duplicating apparatus,
Figure 2 is a planar side view portion of the fusing apparatus of the invention for use in a printing apparatus, and
Figure 3 is a front perspective view of the sump/ribbon mechanism of the fusing apparatus in a printing apparatus.

The key problem for fusing thermoplastic resin or toner images in a color electrophotographic apparatus is good color quality that comes from completely melting colored toners and then cooling it to develop a good fix to the substrate and no offset. The invention uses a mixture of different functionalized release agents to compete for the spectrum of bonding associated with conventional base members. In this manner, the invention provides a fuser member and an apparatus with a fuser member that yield excellent color quality. In the following detailed description, numerous details such as specific materials, structures, dimensions, chemicals, and techniques are set forth in order to provide a more thorough understanding of the invention. It will be appreciated, however, by one of ordinary skill in the art, that these specific details need not be employed to practice the invention. In other instances, well known materials or methods have not been described in detail in order to avoid unnecessarily obscuring the invention.

The invention relates to a fuser member for fusing electrophotographic toner images of various colors. The fuser member includes a base member and a mixture of at least a first polymeric release agent and a second polymeric release agent. Both the first and second polymeric release agents have a functional group selected from the group of hydroxy, epoxy, carboxy, amino, isocyanate, thioether, and mercapto or sulfhydryl. Further, the invention contemplates that the functional group of the first polymeric release agent is different from the functional group of the second polymeric release agent.

The invention also relates to an apparatus with a fuser member for fusing images of various colors. The fuser member of the apparatus includes a base member that is coated with a mixture of at least a first polymeric release agent and a second polymeric release agent. Both the first and the second polymeric release agents have a functional group selected from hydroxy, epoxy, carboxy, amino, isocyanate, and mercapto, and the functional group of the first polymeric release agent is different from that of the second polymeric release agent. The type of functionality of the first and second polymeric release agents will vary depending on the color toners and the base member surface. Typical apparati that can incorporate the fuser member described include, but are not limited to, printers, particularly color laser printers, facsimile machines, and color copying or duplicating apparati.

A typical base member of the invention is described in conjunction with the assembly shown in Figure 1 which is a side view portion of a fuser member of a copier or duplicator apparatus, for example, an electrophotographic copier or duplicator apparatus. Figure 1 shows a base member 4 that is a roller with a substantially cylindrical body portion fabricated from any suitable metal such as aluminum, anodized aluminum, steel, nickel, copper, and the like. The base member 4 has a suitable heating element 6 disposed in a hollow portion of the base member 4 that is coextensive with the substantially cylindrical body. The heating element 6 is used to heat the base member 4 to a temperature of between 50°C and 200°C, preferably approximately 170°C.

The base member 4 in Figure 1 also has a surface 2 that may or may not be of the same material as the base member 4. As used herein, including the discussion of Figure 1 and Figure 2 below, the term base member may be a roller, belt, flat surface, or other suitable shape used in the fixing of thermoplastic toner images to a suitable substrate. Preferably the base member is in the form of a substantially cylindrical roller. Typically, the base member 4 is made of a hollow cylindrical metal core, such as copper, aluminum, steel, and the like. Alternatively, there may be one or more intermediate layers between the substrate and the outer layer of the surface or the surface may be a polymeric cured elastomer if desired. Typical materials having the appropriate thermal and mechanical properties include silicone elastomers, fluoroelastomers, EPDN and Teflon PFA sleeved rollers. Typically, the surface 2 is an elastomer, it is cured

with a curing system, for example, a nucleophilic addition curing system such as bisphenol cross-linking agent with an organophosphonium salt accelerator for a fluoroelastomer base member as described in U.S. Patent Nos. 4,264,181 and 5,017,432. Curing agents and curing techniques for a particular base member are known in the art and are therefore not presented in detail herein.

Pressure roller 8 has a substantially cylindrical body and is positioned adjacent to base member 4 to form a nip or contact arc 10 through which a substrate 12 passes such that latent color toner images 14 on substrate 12 contact elastomer surface 2 of the base member roller 4. The pressure roller 8 has a rigid metal, e.g., steel, core 16 with a polymeric surface layer 18 thereon.

In the embodiment that is a copying or duplicating apparatus shown in Figure 1, a mixture of functionalized polymeric release agents 22 are contained in a sump 20 for applying the mixture to elastomer surface 2. To apply the mixture of the polymeric release agents 22 to the elastomer surface 2, release agent delivery rolls 17 and 19, rotatably mounted in the direction indicated, are provided to transport the mixture 22 from the sump 20 to the elastomer surface 2. As illustrated in Figure 1, roller 17 is partially immersed in sump 20 and transports release agent on its surface from the sump to the delivery roll 19. By using a metering blade 24, a layer of polymeric release agent can be applied initially to delivery roll 19 and subsequently to elastomer 2 in controlled thickness ranging from submicron thickness to a thickness of several micrometers of release agent. It is to be appreciated by one of ordinary skill in the art that there are a number of methods of applying a mixture of release agents to a fuser apparatus of a copier or duplicator and that the invention should not be limited for use with the sump/delivery rolls apparatus described. For example, the delivery sub-apparatus can be a pump, an oiling roller (wherein the roller releases release agent over time), a web, or a wicking device.

The fuser member of the invention is also described in conjunction with the assembly shown in Figure 2 which is a side view portion of a fuser member of a printer apparatus, e.g., an electrophotographic color laser printer apparatus. A similar fuser member can be used in a facsimile machine. Figure 2 shows a base member 40 that is preferably a roller with a substantially cylindrical body portion fabricated from any suitable metal such as aluminum, anodized aluminum, steel, nickel, copper, and the like. The base member 40 has a suitable heating element 60 disposed in a hollow portion of the base member 40 which is coextensive with the substantially cylindrical body. The heating element 60 heats the base member 40 to a temperature of between 50°C and 200°C, preferably approximately 170°C.

The base member 40 has an elastomer surface 20 that may or may not be of the same material as the base member 40. Typically, as with the elastomer layer of the copier apparatus, the elastomer layer 20 of the printing apparatus is cured with a curing system, for example, a nucleophilic addition curing system such as bisphenol cross-linking agent with an organophosphonium salt accelerator for a fluoroelastomer as described in U.S. Patent Nos. 4,264,181 and 5,017,432.

Pressure roller 80 has a substantially cylindrical body and is positioned adjacent to base member 40 to form a nip or contact arc 100 through which a substrate 120 with latent toner images 140 thereon passes such that the toner images contact elastomer surface 20 of the base member roller 40. The pressure roller 80 preferably has a rigid metal, e.g., steel, core 160 with a polymeric surface layer 180 thereon.

In the embodiment that is a printing apparatus shown in Figure 2, a mixture of polymeric release agents with different functionalities 220 is contained in a sump 200 for applying the mixture of the polymeric release agents 220 to elastomer surface 20. To apply the mixture 220 to the elastomer surface 20, release agent delivery web 190 is situated adjacent to transport the mixture of the release agents 220 from the sump 200 to the elastomer surface 20. As illustrated in Figure 2, web 190 advances through sump 200 and retrieves a portion of the mixture and transports on its surface the mixture from the sump 200 to the elastomeric layer 20 of the base member 40 by contacting the elastomeric layer 20 along its length with web 190.

Figure 3 illustrates the delivery mechanism for applying a mixture of release agents 220 of different functionalities to the elastomer surface 20. Figure 3 shows a web 190 attached to a roll 195 that advances the ribbon 190 through sump 200. Sump 200 contains a mixture of polymeric release agents 220 of different functionalities. From the sump 200, the web 190 is coated with a mixture of the release agents 220 and transports the mixture 220 to the elastomeric layer 20 of the base member 40 by contacting the elastomeric layer along its length with the web. The release agent is applied to the elastomeric layer 20 at a conventional thickness known in the art, generally approximately 1 micron or less, or alternatively, expressed as about 0. 1 to about 20 milligrams of release agent per page.

As noted above, the base member of the apparatus of the invention preferably has an outer elastomeric layer that may or may not be of the same material as the base member. The elastomers that may be used in accordance with the invention for the outer layer of the base member must be heat-stable elastomer or resin materials that can withstand elevated temperatures generally from about 90°C up to about 200°C or higher depending upon the temperature desired for fusing or fixing the toner to the substrate. The elastomers used in the invention must further resist degradation or attack by the particular polymeric release agents having functional groups that are used to promote release of the toner from the base member surface. Exemplary of the materials that may be used in accordance with the invention are the silicone elastomers, fluoroelastomer, perfluoroelastomer, fluoro-silicone elastomers, the silicone carborane elastom-

ers, various other silicone rubbers, vinylidene fluoride-based elastomers, various organic rubbers such as ethylene/propylene diene, fortified organic rubbers that resist degradation at fusing temperatures, various co-polymers, blot co-polymers, co-polymer and elastomer blends, fluoropolymers, metal, and the like.

The elastomer surface must have thermal oxidative stability, i.e., resist thermal degradation at the operating temperature of the base member. Thus, the organic rubbers that resist degradation at the operating temperature of the base member may be used in the invention. These include chloroprene rubber, nitrile rubber, chlorobutyl rubber, ethylene/propylene terpolymer rubber (EPDM), butadiene rubber, ethylene/propylene rubber, butyl rubber, butadiene/acrylonitrile rubber, ethylene acrylic rubber, styrene/butadiene rubber, and the like. Resins having similar properties may also be used in accordance with the invention. Examples of suitable resins include, but are not limited to, polytetrafluoroethylene (PTFE), fluorinated ethylene-propylene co-polymer (FEP), and polyfluoroalkoxypolytetrafluoroethylene (PFA Teflon).

Adjuvants and fillers may also be incorporated in the elastomer or resin in accordance with the invention as long as they do not affect the integrity of the elastomer or the interaction between the base member and the polymeric release agent having functional groups. Such fillers normally encountered in the compounding of elastomers and gums include coloring agents, reinforcing fillers, cross-linking agents, processing aids, accelerators, and polymerization initiators. Further, metal containing elastomer materials such as those described in U.S. Patent Nos. 4,272,179 and 4,264,181 can also be used.

The invention contemplates that a mixture of different functionalized polymeric release agents coat the outer surface of the base member to inhibit toner offset and enhance the releasability properties of the apparatus. The release agents that are commonly used to coat the outer surface of the base member are preferably non-volatile. In other words, the release agents do not produce excessive levels of volatile fumes and vapors that penetrate the surrounding atmosphere and cause deposits upon surrounding parts in the copying or printing apparatus. The release agent on the base member should also be thermally stable. To be thermally stable, the agent must not form a gel or decompose at operating temperatures over reasonable periods of time. The release agent is also preferably non-corrosive to the machine parts and to the substrate, and it must be non-reactive or inert to the toner used in the development of the electrostatic latent image. The cohesive strength of a release agent must be less than that of the molten toner so that any interactions between the toner and the release agent will not affect toner release.

Polymeric release agents having functional groups are well known in the prior art and many have been described in the references cited above. The release agents as used in this invention may be a solid or liquid at ambient temperature and a fluid at operating temperatures. The term "polymeric" is understood to be two or more monomer units as a backbone having chemical reactive functional groups attached thereto or attached to side chains and branches of the backbone of the polymer. The reactive functional groups attached to the polymer must be capable of interacting with the base member surface or the elastomer surface of the base member. Furthermore, the polymeric release agents having functional groups must form a thermally-stable film upon the surface of the base member. Release agents that have demonstrated an ability to inhibit offset of toner in the prior art include, but are not limited to, hydroxy-, epoxy-, carboxy-, amino-, isocyanate-, thioether-, and mercapto-functional polymeric release agents. The polymer backbone of these release agents is typically a polyorganosiloxane backbone.

The invention contemplates improved releasability performance with a variety of toners, particularly those toners used in color imaging systems, e.g., copiers, printers, etc. According to the invention, a mixture of functional polymeric release agents distributed over a conventional base member will inhibit interactions between the latent toner and the fuser materials, i.e., base member and release agents. The invention can best be illustrated by a comparison of the invention with conventional fuser members.

The Coupon Test

A test that has been devised to simulate a fusing apparatus and demonstrate the invention is the "coupon" test. The coupon test focuses on the releasability between the fused toner and a heated fuser or base member as a key measure of the image quality of electrophotography. As noted above, two of the important measures of toner fusing quality are the degree of toner offset on a base member and the surface morphology (e.g., smoothness or gloss) of fused toner. The coupon test is designed to assess toner releasability from a fusing material with a release agent.

In the coupon test, the base member is conditioned with a release agent for 18-20 hours at 170°C. The conditioned base member with residual release agent is then brought together with a piece of laser print paper with toner between the paper and the fusing material. This fuser-toner paper sandwich is placed under 1-2 psi pressure at 170°C for ten minutes. The paper is then peeled away from the base member material at about 1 cm/sec. The base member material is examined for toner offset and the fused toner on the laser print paper is examined for fused surface smoothness under an optical microscope. The time duration of the coupon test partially simulates the accumulative effect of toner and release agent on a base member by integrating nip dwell time for the number of prints or copies that the whole fusing system sees in a real machine. The relationship between the test duration and the number of copies in a machine

is,

test duration = no. of copies x nip dwell x no. of rev./copy

As an example, to simulate a machine with a 10 msec. fusing nip dwell time, ten minutes of the coupon test duration time will be equivalent to 60,000 copies if the number of revolutions per copy of the fusing member is 1.

Examples I, II, III, and IV illustrate the toner fuser quality produced by the invention by way of the coupon test.

Example I

Table I illustrates the performance of a variety of fuser materials with different toners. The fuser materials refer to the base member that is a roller with a surface layer and a release agent distributed about the surface layer. The elastomers utilized include a fluoroelastomer (Fluorolast WB, available commercially from Lauren International, Incorporated of New Philadelphia, Ohio), fluoropolymers (Xylan 1010, Xylan 1642, Xylan 8288 available commercially from Whitford Corporation of West Chester, Pennsylvania), and a cross-linked polydimethyl silicone polymer with iron oxides (silicone). The release agents include polydimethyl silicone (PDMS) oil from Dow Corning Corporation at 300 centistoke (cs), mercapto oil with 0.1% SH by weight functional group from Wacker Silicones Corporation of Adrian, Wisconsin, and amino oil of 0.1 meq/g functional group NH_2 also from Wacker Silicones Corporation (311 cs), which is preferably an amino funtionalized tris oxysiloxane.

Toners of very different compositions, properties, and activities were used to illustrate the performance of the fuser materials. The toners used in Table I include M Black which is a polyester resin with chromium complexes of salicylic acid as a charge control agent and silica as surface additives, K2 Black which is a polyester resin with chromium AZO complexes as charge control agents and silica and TiO_2 as surface additives, and K2 Magenta which is a polyester resin with boron and zinc complexes as charge control agents and silica as surface additives. M Black is commercially available from Mitsubishi Chemical Company of Yokohama, Japan. K2 Black and K2 Magenta are commercially available from Kao Corporation of Wakayama, Japan.

Table I illustrates the amount of offset on the base member as well as the fuser toner morphology on the substrate that is a sheet of paper. "100%" offset means the offset has the same size as the fused toner area, "Slight" offset means the offset can be observed under a microscope, "None" offset means no offset can be found under a microscope, "Partial" offset means visual offset with a smaller area than the fused toner area. With regard to the toner morphology on the substrate, "Very Rough" means the fused toner has a tacky- or taffy-pulled surface, "Moderate Rough" means distinct surface features are introduced due to toner release, "Smooth" means the fused toner surface is a replica of the fuser surface, and "Slightly Rough" means that some subtle surface features are introduced due to toner release.

Referring to Table I, it is shown that a toner generally will not be released from a base member with polydimethyl siloxane (PDMS) oil. This suggests that there are interactions between the toner and the fuser material. Table I also shows that one release agent works, i.e., little or no offset and smooth morphology, for one pair of base member and toner but does not work for another pair of base member and toner. Furthermore, a base member without preconditioning with a particular release agent may still yield toner offset. Thus, the role of the release agent is that the release agent must react with the available binding sites on a base member, e.g., a metal roller or metal roller covered by an elastomer layer. This reaction of the release agent with the base member prevents the subsequent reaction between the CCA's or dies of toners with the base member sites. This conclusion differs from that of the conventional view that the release agent must interact with the base member to maintain a barrier layer between the toner and the base member.

Table I also illustrates that the interactions between a fuser material and toner can be rather complex. The very nature of the interactions between a toner and a base member surface depend on the chemical characteristics of the base member surface and the toner. It can be noted in Table I that mercapto oil will block interactions between Fluorolast WB and K2 Magenta toner, but it cannot totally block the interactions between Fluorolast WB and K2 Black toner. In the latter case, the nature of the interaction changes when K2 Black toner replaces K2 Magenta toner. On the other hand, mercapto oil cannot block interactions at all between K2 Magenta toner and Xylan 1642 fluoropolymer. This demonstrates that all the functionalized release agents have different chemical affinities for different materials. For example, mercapto functionality reacts with metals, while hydroxy functionality reacts with isocyanates, ethylene oxide, and various kinds of acids. The effectiveness of a toner release agent, however, lies in its ability to block all interactions between a particular toner and a base member surface. The single release agent mechanism disclosed and relied upon in the prior art is not sufficient to block all the possible interactions between a toner and a base member surface. This is especially true with the different chemical compositions of color toners among Black, Cyan, Magenta, and Yellow toners. The solution to the maintenance of effective toner release performance contemplated by the invention is to blend different functional release agents together to prevent all possible interactions between toners and a particular

base member.

Table I

Fuser Materials	K2 Black	Toner	K2 Magenta	Toner	M Black	Toner
Base Member/ Release Agent	Offset on Fuser	Fused Toner Morphology	Offset on Fuser	Fused Toner Morphology	Offset on Fuser	Fused Toner Morphology
Fluorolast WB/ PDMS oil	100%(1)	very(5) Rough	100%	Very Rough		
Fluorolast WB/ Mercapto oil	Slight(2)	Moderate(6) Rough	None(3)	Smooth(7)		
Fluorolast WB/ Amino oil	None	Moderate Rough	None	Smooth		
Xylan 1642/ PDMS oil	100%	very Rough	100%	Very Rough		
Xylan 1642/ Mercapto oil	100%	very Rough	100%	Very Rough		
Xylan 1642/ Amino oil	None	Smooth	None	Smooth	Slight	Slightly Rough
Xylan 1010/ PDMS oil	100%	Very Rough	100%	Very Rough		
Xylan 1010/ Mercapto oil	None	Smooth	None	Smooth	Slight	Very Rough
Xylan 1010/ Amino oil	None	Slightly(8) Rough	None	Slightly Rough	Partial	Very Rough
Xylan 8288/ PDMS oil	100%	Very Rough	100%	Very Rough		
Xylan 8288/ Mercapto oil	Slight	Moderate Rough	None	Moderate Rough		
Xylan 8288/ Amino oil	None	Moderate Rough	None	Smooth		
Silicone/ PDMS oil	Partial(4)	Moderate Rough	Partial	Moderate Rough	Slight to None	Moderate Rough

The invention uses a mixture of functional polymeric release agents to provide better releasability than an individual functional release agent used alone to interact with a base member. The functional polymeric release agents that have been shown to be effective to inhibit toner offset when used alone are those polymeric release agents that have a functional group selected from hydroxy, epoxy, carboxy, amino, isocyanate, and mercapto. By blending a mixture of these agents properly, the mixture offers toner releasability to a base member or fuser member with a wide range of elastomeric layer materials and toners of various chemical compositions. The suitable mixture will chemically bind to available binding sites on the base member surface and inhibit toner/base member interacting.

Example II

Table II illustrates the results of the coupon test with a base member with an outer fluoroelastomeric layer (Fluorolast WB available commercially from Lauren International, Incorporated) covered with a coating of individual polymeric

functional release agents and a combination of polymeric release agents. The polymeric functional release agents used in this example are mercapto-functional oil with 0.1% -SH functionality, commercially available from Wacker Silicones Corporation of Adrian, Wisconsin, and amino-functional with 0.1 meq/g-NH_2 functionality also from Wacker Silicones Corporation (311 cs). Two different toners, K2 Black and K2 Cyan, commercially available from Kao Corporation of Wakayama, Japan, are used to demonstrate the release effectiveness. The results of the coupon test, shown in Table II, illustrate that with a fluoroelastomer covered base member and a mercapto-functional release agent, slight offset on the elastomer surface of the base member can be seen and the morphology on the paper is moderately rough indicating distinct surface features are introduced due to toner release with the K2 Black toner. With the K2 Cyan toner, on the other hand, no toner offset is seen on the elastomeric base member and a smooth toner morphology is seen on the paper. With the same base member and an amino-functional release agent, there is very slight offset on the base member with the K2 Black toner and the surface morphology of the paper is moderately rough. On the other hand, with the K2 Cyan toner, there is no offset on the base member and the morphology is smooth. A mixture of about 0.05% SH by weight mercapto-functional and about 0.05 meq/g NH_2 amino-functional release agents on the fluoroelastomer base member demonstrate no toner offset and smooth toner morphology with both the K2 Black toner and the K2 Cyan toner. A mixture of about 0.075% SH by weight mercapto-functional and about 0.025 meq/g NH_2 amino-functional release agents on the fluoroelastomer base member demonstrate no toner offset and a slightly rough toner morphology with the K2 Black toner and no toner offset and smooth toner morphology with the K2 Cyan toner. Thus, Example II demonstrates that a mixture of different functional release agents, namely mercapto- and amino-functional release agents, in various combinations, yields hetter releasing properties with different compositions of toner than when either release agent is used singularly. It follows that mixtures of other effective, offset-inhibiting release agents, including mixtures of two or more release agents with different functionalities, will also yield better releasing properties than any release agent used singularly with multiple toners.

Table II

Fuser Materials	K2 Black	Toner	K2 Cyan	Toner
Base Member/ Release Agent	Offset on Fuser	Fused Toner Morphology	Offset on Fuser	Fused Toner Morphology
Fluorolast WB/ Mercapto, 0.1% SH by Weight	Slight	Moderate Rough	None	Smooth
Fluorolast WB/Amino, 0.1 meq/g Amine number	v. slight	Moderate Rough	None	Smooth
Fluorolast WB/ Mercapto, 0.05% SH by Weight And Amino 0.05 meq/g Amine number	None	Smooth	None	Smooth
Fluorolast WB Mercapto 0.075% SH by Weight Amino 0.025 meq/g Amine number	None	Slightly Rough	None	Smooth

Example III

In this example of the coupon test described above, a base member with a fluoropolymer outer layer (Xylan 8288 commercially available from Whitford Corporation of West Chester, Pennsylvania) is coated with an individual polymeric functional release agent (mercapto- and amino-functional) and a mixture of functional release agents (mercapto- and amino-functional). Table III illustrates that with K2 Black toner, the mercapto-functional release agent yields a slight toner offset and a moderately rough toner morphology. The K2 Cyan toner shows no toner offset on the base member but a moderately rough toner morphology on the paper. The amino-functional release agent yields no toner offset with the K2 Black toner and a moderately rough morphology. The amino-functional release agent yields no toner offset with the K2 Cyan toner and a smooth toner morphology. A mixture of about 0.05% SH by weight mercapto- and about 0.05 meq/g amine number amino-functional release agents on a fluoropolymer base member yields no toner offset with the

K2 Black toner and a slightly rough toner morphology. The same combination yields no toner offset and a smooth toner morphology with the K2 Cyan toner. Example III demonstrates again that a mixture of polymeric functional release agents yields better offset and toner morphology with various toners than a release agent having singular functionality.

Table III

Fuser Materials	K2 Black	Toner	K2 Cyan	Toner
Base Member/ Release Agent	Offset on Fuser	Fused Toner Morphology	Offset on Fuser	Fused Toner Morphology
Xylan 8288/Mercapto oil 0.1% SH by Weight	Slight	Moderate Rough	None	Moderate Rough
Xylan 8288/Amino oil 0.1 meq/g Amine number	None	Moderate Rough	None	Smooth
Xylan 8288/Mercapto 0.05% SH by Weight and Amino 0.05 meq/g Amine number	None	Slightly Rough	None	Smooth

Example IV

Table IV illustrates the results of the coupon test with a base member with an outer fluoropolymer layer covered with a coating of individual polymeric functional release agents and a combination of polymeric release agents. The polymeric functional release agents used in this example are mercapto-functional oil with 0.1% by weight -SH functionality, available commercially from Wacker Silicones Corporation and carbinol-functionality with 0.355% by weight -OH functionality, available commercially from Genesee Polymers Corporation of Flint, Michigan. Two different toners, M Black and M Cyan (commercially available from Mitsubishi Chemical Company) are used to demonstrate the release effectiveness. The results of the coupon test, shown in Table IV, illustrate that with a fluoropolymer covered base member and a mercapto-functional release agent, partial offset on the fluoropolymer surface of the base member can be seen and the morphology on the paper is very rough, indicating tacky or taffy-dull surface features with the M Black and M Cyan toners. With the same base member and a carbinol-functional release agent, there is no offset on the base member with the M Black toner and the surface morphology of the paper is moderately rough. On the other hand, with the M Cyan toner, there is partial offset on the base member and the morphology is very rough. A 0.05%:0.18% weight ratio of mercapto-functional and carbinol-functional release agent on the fluoropolymer base member demonstrate no toner offset with both the M Black and M Cyan toners, a smooth toner morphology with the M Black toner and a slightly rough toner morphology with the M Cyan color toner. Thus, Example IV demonstrates that a mixture of different functional release agents, namely mercapto- and carbinol-functional release agents, yields better releasing properties with different compositions of toner than when either release agent is used singularly.

Table IV

Fuser Materials	M Black	Toner	M Cyan	Toner
	Offset on Base member	Fused Toner Morphology	Offset on Base member	Fused Toner Morphology
Xylan 8288 Mercapto oil 0.1% SH by Weight	Partial	Very Rough	Partial	Very Rough
Xylan 8288 Carbinol oil 0.355% OH by Weight	None	Moderate Rough	Partial	Very Rough
Xylan 8288 Mercapto 0.05% SH by Weight and Carbinol 0.18% OH by Weight	None	Smooth	None	Slightly Rough

Example V

Example V measures the finished gloss on a substrate in a printing apparatus. The finished gloss on the substrate depends on fusing temperature. Any disturbance to the fused toner surface is due to toner release. However, high temperature results in high gloss, because toner melt has low viscosity at high temperature and the fused surface relaxes to form a smoother surface on the paper. Low fusing temperature usually results in low gloss, because toner melt has high viscosity and the fused surface does not relax sufficiently. In short, the gloss will be less dependent on temperature if the fused toner surface can be released from the base member with little or no disturbance.

Tests are done in a Tektronix Phaser® 550 color laser printer in 600 dots per inch (dpi) mode. Three base members were coated with amino-functional release agent, mercapto-functional release agent and a mixture of amino- and mercapto-functional release agents, respectively. The base members were conditioned in amino-functional, mercapto-functional and the mixture of amino- and mercapto-functional agents, respectively, for about 20 hours at about 170°C. The fuser roll starting temperature has a variation of about ± 7°C. The fuser roll surface temperature drops about 5-7°C within a page.

A 45° Glossard-2 glossmeter, available commercially from BYK-Gardner of Silver Springs, Maryland was used to measure the 45° gloss on solid black prints (K2 toner) from the three base members using different release agents. Since the fusing temperature fluctuates between prints, direct comparison between prints cannot be made. However, the temperature drop within a print is constant. Thus, the difference between the gloss at the leading edge of the print and the trailing edge of the print (ΔG) is an indicator of the effectiveness of the toner release. A lower ΔG is desirable, the lower value indicating a more effective toner release.

Table V demonstrates that the amino- and mercapto-functional mixture provides the most uniform finished gloss where there is about a 5-7°C fuser temperature drop between the leading edge and the trailing edge of a page (3.0 average compared to 6. 1 and 11.9 average of individual release agents). This result indicates that the mixture of the two release agents facilitates more effective toner release in comparison with either amino- or mercapto-functional release agent used alone.

Example V:

Table V

Fuser	G Trial 1	G trial 2	G trial 3	G trial 4	G trial 5	Average
Amino and Mercapto	1.0	5.4	3.2	2.4	3.1	3.0
Amino	6.3	6.1	7.0	4.6	6.7	6.1
Mercapto	3	13.6	na	17.5	13.6	11.9

The examples above demonstrate the complexity of the interaction between the toner material and the fuser apparatus. While effective release agents have been developed for particular base members to be used on a particular toner, few if any have been shown to be effective with different or multiple toners. With the advent of color printing and copying or duplicating, the fuser apparatus encounters multiple thermoplastic toners with a variety of properties that effect the interaction between the toner and the base member (e.g., polymer resin, CCAs, pigments, dyes, additives). These toners have individual properties that demonstrate activity for particular binding sites on base members, with or without elastomeric surfaces. Accordingly, it is important that release agents bind with any available site on the base member that might otherwise chemically interact with the toner to cause offset. In accordance with the invention, a mixture of two or more polymeric release agents has proven effective to occupy the available binding sites on the base members. Further, this mixture of two or more release agents has proven effective to diminish the Van der Waals or other attractive forces between the toner and the base member that might otherwise produce offset.

While the detailed description in accordance with the invention has been set forth above with regard to the best mode and preferred embodiment or embodiments contemplated by the inventor, it is to be appreciated that the invention is not limited to the above embodiment or embodiments and that various modifications may be made to the above embodiment or embodiments without departing from the scope of the invention. For example, the amino- and mercapto-functional oil coating may be applied to the base member or roller either as a premixed mixture or a separate application coatings that mix on the base member or roller. The specific embodiment or embodiments are, accordingly, to be regarded in an illustrative rather than a restrictive sense.

Claims

1. A fuser member (1, 9) for fusing electrophotographic toner (14,140) images of various colors comprising:

   a base member (4, 40) having a surface (2, 20);
   a first polymeric release agent having a functional group selected from hydroxy, epoxy, carboxy, amino, isocyanate, thioether, or mercapto; and
   at least a second polymeric release agent having a functional group selected from hydroxy, epoxy, carboxy, amino, isocyanate, thioether or mercapto,

   wherein said surface (2, 20) of said base member (4, 40) is coated with said first polymeric release agent and said second polymeric release agent, and wherein said functional group of said first polymeric release agent is different from said functional group of said second polymeric release agent.

2. A fuser member (1, 9) as claimed in claim 1, wherein said functional group of said first polymeric release agent is amino and said functional group of said second polymeric release agent is mercapto.

3. A fuser member (1, 9) as claimed in claim 2, wherein said first polymeric release agent and said second polymeric release agent are present in approximately equal amounts by weight.

4. A fuser member (1, 9) as claimed in claim 1, wherein said functional group of said first polymeric agent is hydroxy and said functional group of said second polymeric release agent is mercapto.

5. A fuser member (1, 9) as claimed in any previous claim, further comprising a third polymeric release agent.

6. A fuser member (1,9) as claimed in claim 5, wherein said third polymeric release agent has a functional group selected from hydroxy, epoxy, carboxy, amino, isocyanate, thioether or mercapto, and wherein said functional group of said third polymeric release agent is different from said functional group of said first polymeric release agent and different from said functional group of said second polymeric release agent.

7. A fuser member (1, 9) as claimed in any previous claim, wherein said surface (2, 20) is constituted of a first material and wherein said first material of said surface comprises an elastomer, a resin or a fluoropolymer.

8. A fuser member (1, 9) as claimed in claim 7, wherein the said material of said surface comprises an elastomer selected from silicone elastomers, fluoroelastomers, perfluoroelastomers, or fluorosilicone elastomers.

9. A fuser member (1, 9) as claimed in any previous claim, wherein said base member (4, 40) has a substantially cylindrical body and wherein said fuser member (1, 9) further comprises a pressure roller (8, 80) having a substantially cylindrical body (16, 160) adjacent to said base member (4, 40) such that said base member (4, 40) and said pressure roller (8, 80) define a contact arc (10, 100) to fuse toner images (14, 140) on to a substrate (12, 120) passing between said base member (4, 40) and said pressure roller (8, 80).

10. A fuser member as claimed in any previous claim, wherein said surface (2, 20) of said base member (4, 40) has a plurality of chemically reactive binding sites and wherein said functional group of said first polymeric release agent and said functional group of said second polymeric release agent bind to said sites of said base member (4, 40).

11. An apparatus with a fuser member (1, 9) for fusing images of various colors wherein the fuser member is a fuser member as claimed in any preceding claim.

12. An apparatus as claimed in claim 11 wherein the base member contains a heating means.

13. An apparatus as claimed in claim 11 or claim 12 which is a printing apparatus, a copying apparatus or a facsimile apparatus.

14. An apparatus as claimed in claim 13 which is an electrophotographic printing apparatus, an electrophotographic copying apparatus or an electrophotographic facsimile apparatus.

15. A fusing apparatus (1, 9) for fusing electrophotographic toner images of various colors (14, 140) on a substrate (12, 120) in an imaging apparatus comprising:

a heated base member (4, 40) having a substantially cylindrical body and a surface (2, 20), said surface (2, 20) constituted of a material selected from an elastomer, a resin or a fluoropolymer;
a pressure member (8, 80) having a substantially cylindrical body adjacent to said base member (4, 40) such that said base member (4, 40) and said pressure roller (8, 80) define a contact arc (10, 100) to fuse toner images (14, 140) on said substrate (12, 120) passing between said base member (4, 40) and said pressure roller (8, 80);
a first polymeric release agent having a functional group selected from hydroxy, epoxy, carboxy, amino, isocyanate, thioether or mercapto; and
at least a second polymeric release agent having a functional group selected from hydroxy, epoxy, carboxy, amino, isocyanate, or mercapto,

wherein said surface (2, 20) of said base member (4, 40) is coated with a mixture of said first polymeric release agent and said second polymeric release agent, and wherein said functional group of said first polymeric release agent is different from said functional group of said second polymeric release agent.

16. An apparatus as claimed in claim 15 which is a printing device, a copying device or a facsimile device.

17. A composite polymeric release agent comprising a mixture of a first polymeric release agent having a functional group selected from hydroxy, epoxy, carboxy, amino, isocyanate, thioether or mercapto; and at least a second polymeric release agent having a functional group selected from hydroxy, epoxy, carboxy, amino, isocyanate, thioether or mercapto, where said function group of said first polymeric release agent is different from said functional group of said second polymeric release agent.

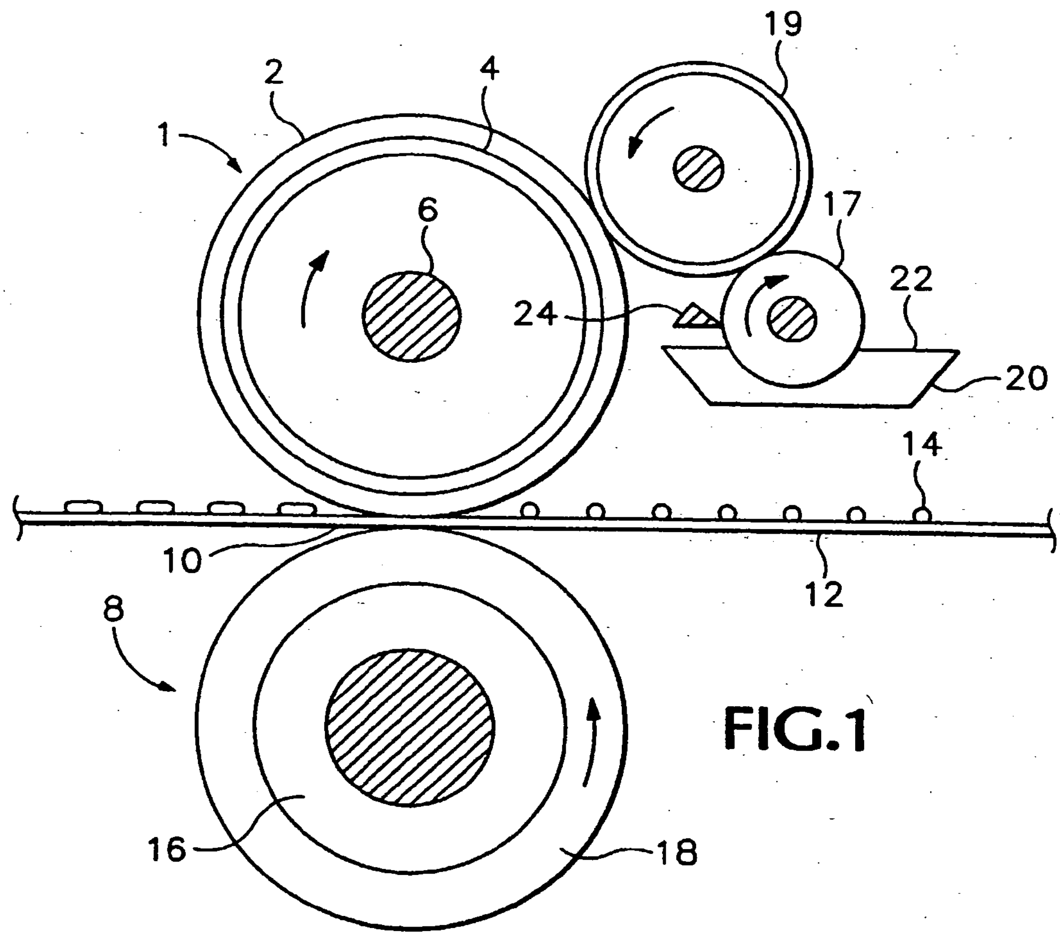

FIG.1

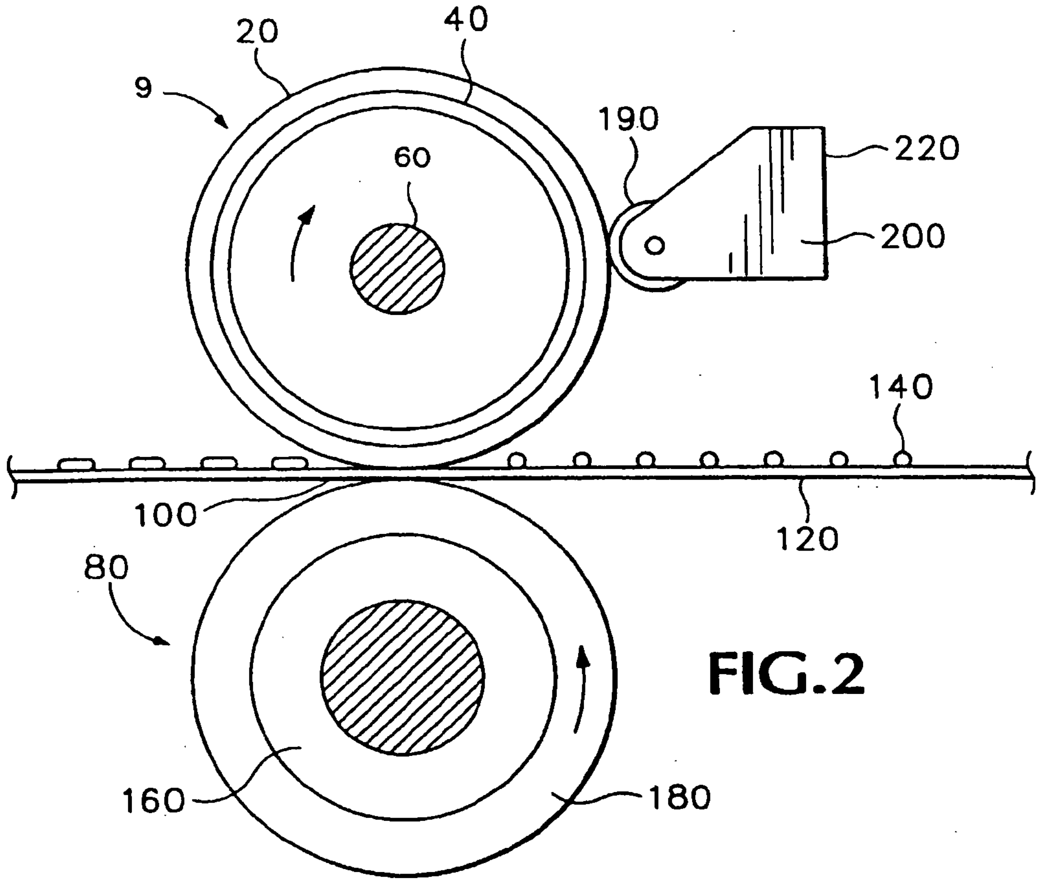

FIG.2

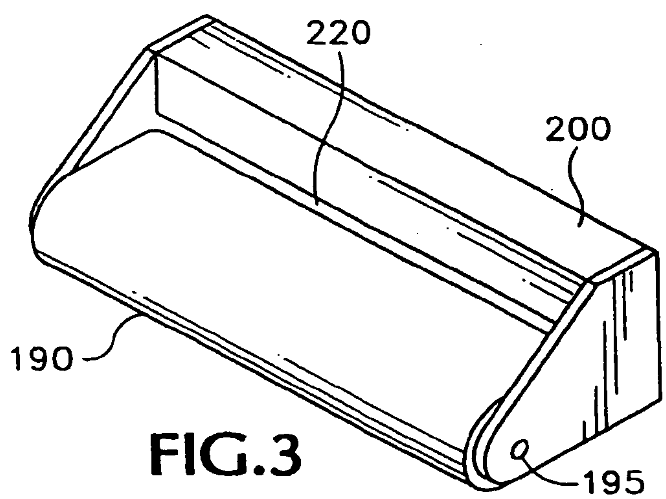

FIG.3

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 869 406 A3

(12) EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
05.07.2000 Bulletin 2000/27

(51) Int Cl.7: G03G 15/20

(43) Date of publication A2:
07.10.1998 Bulletin 1998/41

(21) Application number: 98302295.5

(22) Date of filing: 24.03.1998

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 01.04.1997 US 831990

(71) Applicant: TEKTRONIX, INC.
Wilsonville, Oregon 97070-1000 (US)

(72) Inventor: Ni, Beta Y.
Sherwood, Oregon 97140 (US)

(74) Representative:
Lawrence, Malcolm Graham et al
Hepworth, Lawrence, Bryer & Bizley
Merlin House
Falconry Court
Baker's Lane
Epping Essex CM16 5DQ (GB)

(54) Fusing apparatus employing multi-fuctional toner release agent

(57) The invention relates to a fuser member (1,9) and an apparatus with a fuser member for fusing electrophotographic toner images of various colors (14, 140) to a substrate (12, 120). The fuser member (1, 9) includes a base member (4, 40) coated with a mixture of at least a first and a second polymeric release agent. The first and second polymeric release agents each have a functional group selected from hydroxy, epoxy, carboxy, amino, isocyanate, thioether, or mercapto. The functional group of the first polymeric release agent is different from the functional group of the second polymeric release agent. The functional groups of the first and second polymeric release agents occupy through reactive binding sites on the surface of the base member.

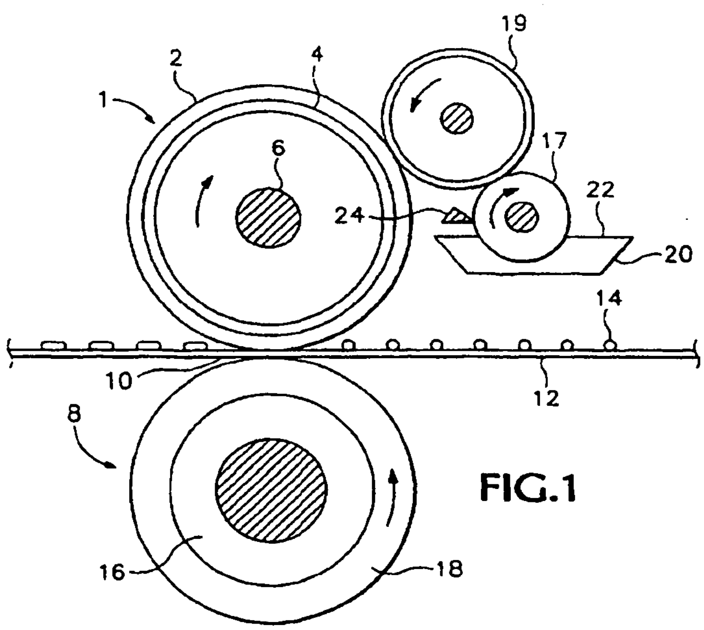

FIG.1

EP 0 869 406 A3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 30 2295

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X Y A	US 4 185 140 A (HOFFEND THOMAS R ET AL) 22 January 1980 (1980-01-22) * abstract; claims *	1,9,17 5-8 2-4,15, 16	G03G15/20
Y A	US 5 157 445 A (FUKASE YASUJI ET AL) 20 October 1992 (1992-10-20) * claims *	5-8 4,9,10, 12-16	
D,A	US 4 272 179 A (SEANOR DONALD A) 9 June 1981 (1981-06-09) * claims *	1-17	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	15 May 2000	Lipp, G

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 98 30 2295

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-05-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4185140 A	22-01-1980	US 4101686 A	18-07-1978
		BE 831662 A	17-11-1975
		CA 1110510 A	13-10-1981
		DE 2526083 A	12-02-1976
		FR 2280116 A	20-02-1976
		GB 1507496 A	12-04-1978
		JP 1231882 C	26-09-1984
		JP 51036141 A	26-03-1976
		JP 59004699 B	31-01-1984
		NL 7506978 A,C	29-08-1975
US 5157445 A	20-10-1992	DE 4112062 A	17-10-1991
		GB 2242863 A,B	16-10-1991
		JP 2900637 B	02-06-1999
		JP 4230784 A	19-08-1992
		US 5250996 A	05-10-1993
US 4272179 A	09-06-1981	CA 1133330 A	12-10-1982
		DE 3068768 D	06-09-1984
		EP 0018140 A	29-10-1980
		JP 1006464 B	03-02-1989
		JP 1521600 C	12-10-1989
		JP 55135877 A	23-10-1980

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82